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Disposal Methods: Landfills, Geologic Formations, Chemical Stabilization, and Chemical Treatment

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Introduction

This section will deal with four hazardous waste disposal options, i.e., landfills, geologic formations, chemical stabilization, and chemical treatment. Landfilling has been the traditional method of disposing of hazardous waste. Improper land disposal has led to numerous cases of ground- and surface-water pollution. As a result of environmental damages created by poorly designed landfills, Congress placed stringent criteria on landfills when it passed "The Hazardous and Solid Waste Amendments of 1984.[1] For this chapter, geologic formation disposal will include the placement of hazardous waste in injection wells, salt formations, and underground mines. Chemical stabilization/solidification will include processes that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. Chemical treatment comprises a set of technology tools used to prevent the release of hazardous materials into the environment, or to alter their nature so they are no longer an environmental problem.

Landfills

A Task Force report by the American Institute of Chemical Engineers[2] drew some thought-provoking conclusions about landfills:

> "Use of impoundments and landfills for the management of hazardous waste is greatly affected by two somewhat conflicting facts: (1) there will always be a need to dispose of residues in the environment; and

(2) all land disposal schemes are ultimately subject to some form of failure in terms of releases of contaminants to the environment. The first statement is true by virtue of the fact that some toxic constituents cannot be destroyed, do not have sufficient utility in commerce for recycle, and their production cannot be eliminated by process modification.-----The second statement has been hotly debated, but cannot be denied if a sufficiently long-term view is taken.----- Hazardous waste management in the future should be based on two guiding principles: (1) the volume and/or intrinsic hazard of wastes requiring ultimate disposal should be minimized; and (2) ultimate disposal technology should be designed to minimize the effects of anticipated failure modes."

The 1984 amendments to the Resource Conservation and Recovery Act placed significant restrictions on those wastes that can be disposed into landfills, and on minimum technology requirements for landfill design, construction, and operation. The numerous cases of groundwater pollution[3] that have been reported as a result of poorly designed and operated landfills led to a dual approach to decreasing the environmental risk associated with landfills. The first approach is to ban landfilling of hazardous wastes that have long-term uncertainties associated with them. Banning of waste would be based on the persistence, toxicity, mobility, and propensity to bioaccumulate. In other words, there are hazardous wastes that, due to their characteristics, are unsuitable for landfills and the undesirable characteristics must be removed before landfilling would be permissible. The second approach is to construct and operate landfills so that hazardous substances are not released to the environment, and to monitor landfills so that corrective actions can be taken if releases occur.

Placement of liquids into landfills is felt to be undesirable because of the potential for liquids to migrate, and the liquids may leach other wastes within the landfill and cause them to migrate. Because of these concerns, as of May 8, 1985, the disposal of bulk or noncontainerized liquid hazardous wastes or free liquids contained in hazardous waste is prohibited. In addition, EPA has promulgated regulations that minimize the disposal of containerized hazardous liquid waste. These regulations prohibit the disposal of liquids that are absorbed in materials that biodegrade or release liquids when compressed during routine landfill operations.

EPA is developing a list of specific wastes that are prohibited from being landfilled based on the criteria previously given. The first wastes considered for banning will be dioxin-containing wastes and spent or discarded solvents. A decision by EPA must be made by November 1986 or these wastes will be automatically banned. The second group to be considered for banning is referred to as the "California List" (Table 1) and EPA must make its determination on banning by July 1987.

TABLE 1

CALIFORNIA LIST OF HAZARDOUS WASTES*

Free Cyanides	≥ 1,000 mg/l	Lead	≥ 500 mg/l
PCB	≥ 50 mg/l	Mercury	≥ 20 mg/l
pH	≤ 2.0	Nickel	≥ 134 mg/l
Arsenic	≥ 500 mg/l	Selenium	≥ 100 mg/l
Cadmium	≥ 100 mg/l	Thallium	≥ 130 mg/l
Chromium VI	≥ 500 mg/l		

*Banning concentration

EPA is to review and rank all other listed or identified hazardous wastes and make a banning determination by May 1990.

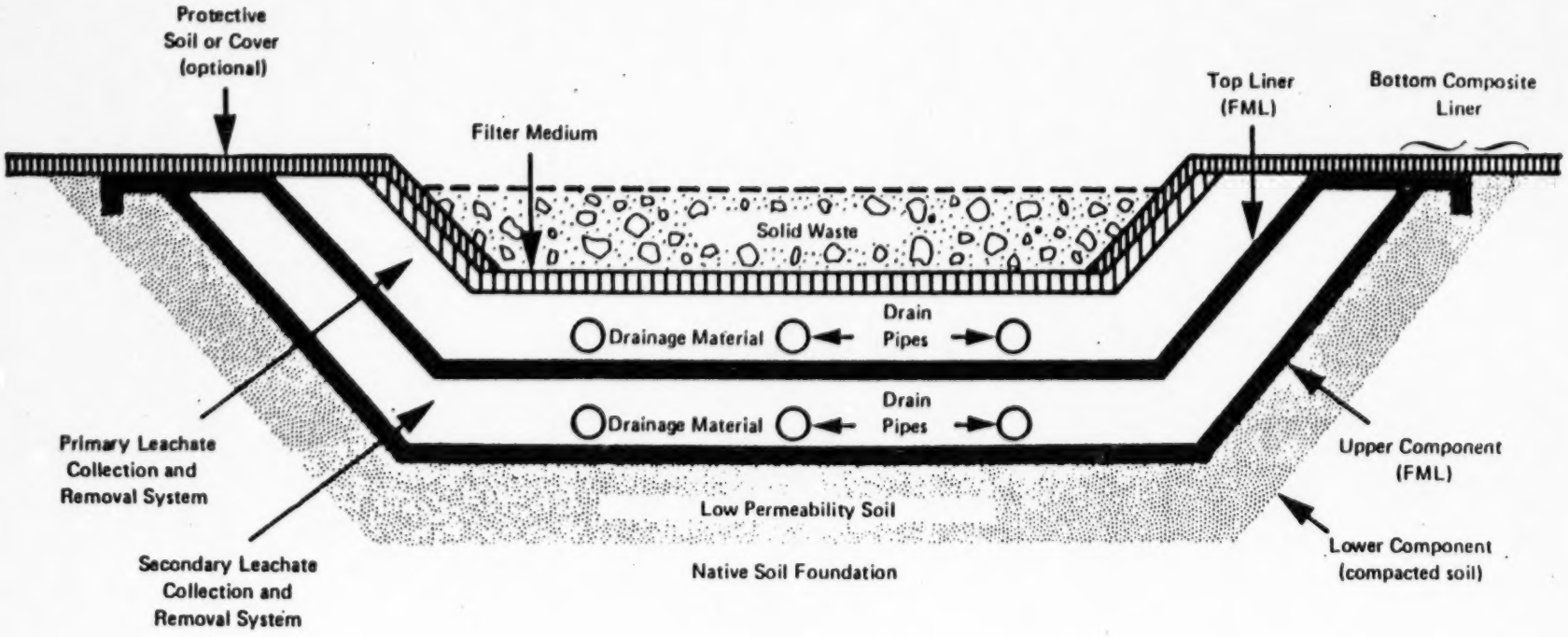
Land disposal of these wastes, even if they are on the banning list, is possible if the wastes are pretreated to specific levels or standards that will be established by EPA, or the disposer can demonstrate to EPA or the State Regulatory Agency that land disposal of the waste will protect human health and the environment.

The second approach to insure that landfills do not create environmental damages is "Minimum Technology Requirements." Beginning in May 1985, new landfills must have double liners, leachate collection systems above and beneath the liners, and groundwater monitoring systems.

The principle behind landfill design and operation is that during the active life of a landfill the bottom will be lined to prevent or minimize the release of leachates. Any moisture that enters the landfill from precipitation or the waste is collected in a leachate collection system and removed to a treatment system.[4] Once the landfill has been filled, a cover is placed over the landfill to prevent moisture from entering. If the cover is operating properly, in time free liquids that may be in the landfill will be removed and leachate production will cease. Thus, the key to a successful landfill is proper design, installation, and maintenance of liner and cover systems.

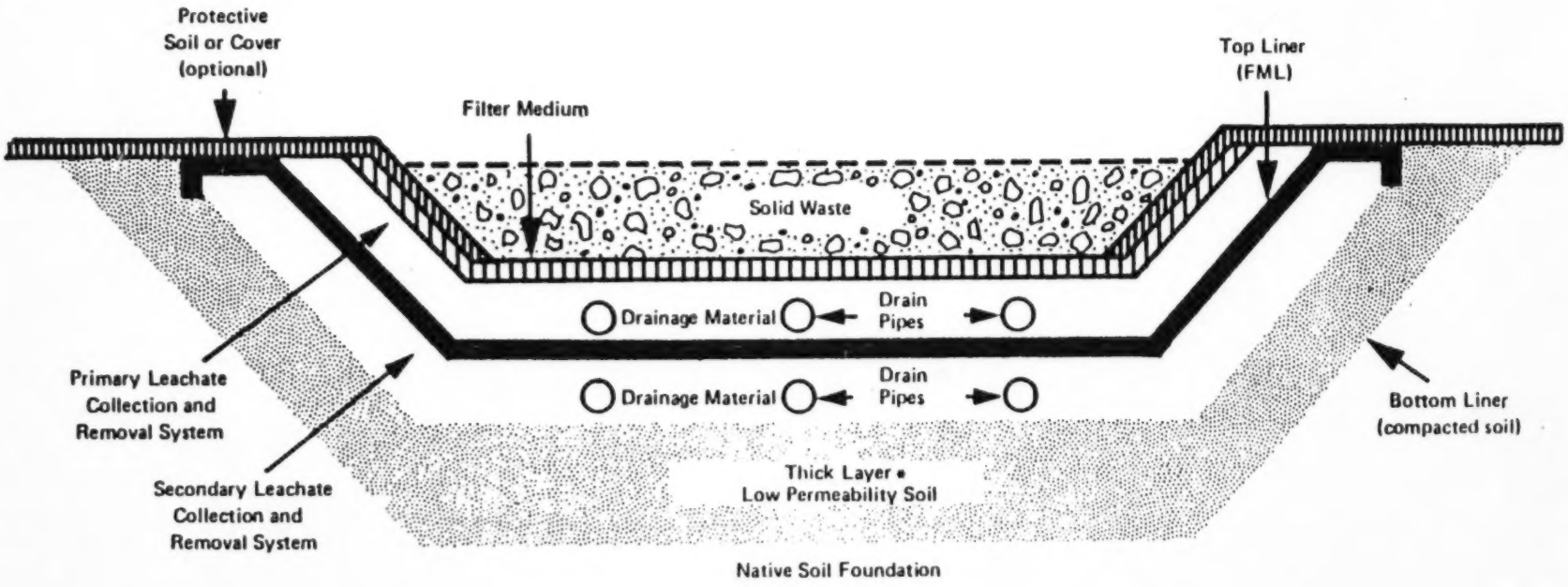
Figures 1 and 2 illustrate the double liner concepts now required to meet the Hazardous and Solid Waste Amendments. In essence, the double liner system is a redundant liner system. If the first liner fails, then there is a second one to protect the environment. In addition, there is a leachate collection system between the two liners that also serves as a leak detection system. Liners are constructed of two primary materials: (1) flexible membrane

FIGURE 1
SCHEMATIC OF AN FML/COMPOSITE DOUBLE LINER SYSTEM
FOR A LANDFILL



(Not to Scale)

FIGURE 2
SCHEMATIC OF AN FML/COMPACTED SOIL DOUBLE LINER SYSTEM
FOR A LANDFILL



• Thickness to be determined by break through time.

(Not to Scale)

liners (FML's), and (2) low-permeability soil. The EPA has prepared several documents on the use of clay and flexible membranes as liners.[5,6,7,8,9]

Intact flexible membrane materials are impermeable to liquids though some solvents may diffuse slowly through the membrane. A wide variety of FML materials is being manufactured and marketed. These materials vary considerably in physical and chemical properties, methods of installation, costs, and resistance to various wastes. The durability and service life of a given FML depend to a great extent on the specific liquids that contact the liner. No single FML material can resist chemical attack by all wastes. The compatibility of a liner with a specific waste is one of the first considerations a designer has in planning a specific landfill site. Table 2 lists the principal failure mechanisms in liners. Each of these factors must be considered in the design of the liner. However, even the best design suffers if the installation lacks proper quality assurance.[10] Probably more liners fail from improper installation than improper selection of FML materials or design.

Low-permeability soils have been a common liner material for years. However, it must be realized that all soils have some finite leakage rate. For example, soils with a permeability of 1×10^{-7} centimeters/second (a value commonly recommended for liners) would have a seepage rate of 79 gallons/acre/day under a 1-foot head. Thus, in the design of a soil liner, the capacity of the environment surrounding the landfill to assimilate the leakage safely must be considered. The suitability of a soil as a liner material is usually based on laboratory permeability testing. There is evidence that permeabilities measured in the field are higher than those found in the laboratory because the rigorous laboratory conditions cannot be duplicated in the field. There also is evidence that wastes, especially concentrated wastes, interact with the soil causing an

TABLE 2[8]

FAILURE MECHANISMS FOR FML's

Physical	Biological	Chemical
Puncture	Microbial attack	Ultraviolet attack
Tear		Ozone attack
Creep		Hydrolysis
Freeze-thaw cracking		Ionic species attack
Wet-dry cracking		Extraction
Differential settling		Ionic species incompatibility
Thermal stress		Solvents
Hydrostatic pressure		
Abrasion		

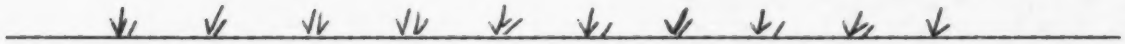
increase in permeability. Thus, it is recommended that permeability tests be conducted with the waste/leachate that will be present in the landfill.[11,12,13,14,15,16,17]

Covers are similarly multi-layered systems. The landfill cover is designed to exclude surface waters from contacting the landfilled waste, to act as a barrier to human or animal contact with the waste, and to prevent uncontrolled releases of vapors to the environment.

Figure 3 presents a schematic diagram of the elements that may be found in a multi-layered cover system. All systems need a surface layer for vegetative support and protection of the hydraulic barrier. An FML hydraulic barrier is used to control water percolation. A gas control layer intercepts gases

FIGURE 3

STRUCTURE OF A COVER SYSTEM



SURFACE (VEGETATIVE SUPPORT)

FILTER(S)

BIOTIC BARRIER

DRAINAGE

FML HYDRAULIC BARRIER

FOUNDATION (BUFFER)

FILTER(S)

GAS CONTROL

WASTE

generated by the wastes and conducts them to the atmosphere by means of venting mechanisms. A foundation or buffer layer isolates the hydraulic barrier from the wastes and also provides mechanical strength needed to support the rest of the system. A drainage layer intercepts downward-percolating water and conveys it laterally out of the system. A biotic-barrier layer (largely conceptual at present) hinders plant roots and burrowing animals from disrupting the layers below, particularly the hydraulic barrier. Filter layers serve to separate fine from coarse materials and to prevent clogging of drainage layers by fine particles.[18,19,20]

Geologic Formations

Geologic formations have been used for the disposal/storage of hazardous waste. Injection wells have been a popular disposal method for some time. In 1981, an estimated 2.8 percent of the chemical industry's hazardous wastes were disposed in this manner.[21] The long-term or permanent storage of hazardous waste in underground mines has been proposed for a number of years. The EPA has conducted a number of feasibility studies on the subject which have shown it to be a viable option.[22] Only one underground mine currently is being used, i.e., a salt mine in West Germany. In recent years there have been several proposals to use salt domes for hazardous waste disposal. These proposals include use of existing cavities and solution mining of new cavities.

Injection Wells

Injection well disposal involves injection of liquid waste into subsurface geologic formations by means of wells. The technique is based on the concept that liquid wastes can be injected into and contained by geologic strata that do not have any potential beneficial uses. This practice is used widely by the

oil industry to dispose of brine. Since the 1950's, there has been a steady increase in the use of wells for disposal of other industrial waste. Over 250 wells containing 150 different chemical compounds are now operating. Injection well disposal is not without controversy. Proponents argue that it is a safe, economical method to dispose a variety of wastes, while opponents are concerned with groundwater pollution and future use of the aquifer. Some states have limitations on the types of wastes that can be injected, for example, chlorinated hydrocarbons.

The geologic formation is the key factor in injection wells. Desirable factors for an underground reservoir are: uniformity, large areal extent, substantial thickness, high porosity and permeability, low pressure, a salaquifer (an aquifer containing brackish water, salt water, or brine), separation from fresh-water horizons, adequate overlying and underlying aquicludes (a stratum that confines water), no poorly plugged wells into the reservoir, and compatibility between the mineralogy and fluids of the reservoir and the injected waste. Those injection wells that have created environmental problems have been located in unsuitable geologic settings or have been poorly engineered and installed for the geologic conditions present. Good engineering and construction of an injection well are critical to its success. The first concern in planning, construction, and operation is the protection of potable waters and minerals of economic value. The second concern is the possibility of corrosion of the tubular works and cementitious materials used in well construction.

Underground Storage

At this time the USEPA has no regulations concerning underground mine storage of hazardous waste. The 1984 amendments to RCRA prohibit the disposal

of bulk or noncontainerized liquid hazardous waste in salt domes, salt beds, underground mines, and caves as of November 8, 1984, until the USEPA promulgates performance and permitting standards for such facilities. For underground mine storage, the hazardous waste is packed in a solid form, transported into the mine, and placed in prepared rooms. The disposal areas are segregated to contain wastes that are compatible with one another. Rooms are filled and then sealed off. If the mine is selected properly, the atmosphere is very dry and the drums have an indefinite life unless they are corroded from the inside. One advantage of this system is that waste can be retrieved at a later date, if necessary. Salt, potash, and gypsum deposits have been identified as having the greatest potential for waste storage. Salt deposits have many advantages including their wide distribution throughout the United States, making them likely to be within close proximity to industrial areas.

Although several firms in the United States have considered mine disposal, none are currently in operation. The Herfa-Neurode facility in the Republic of West Germany has run satisfactorily since its startup in 1972. About 270,000 tons of hazardous wastes were placed in the mine over 10 years, and the present annual volume is 35,000 to 40,000 tons. Reuse of stored waste is possible, and more than 1,000 tons have been retrieved.

The basic technique for developing a salt dome cavern solution mine is to drill into a salt mass and to pump fresh or low-salinity water into the hole. The salt is then dissolved and carried to the surface as a brine solution. The void within the exposed salt gradually enlarges and eventually forms a useful cavern.

Solution-mined caverns could provide suitable containment facilities for hazardous wastes and good isolation from the environment. After the waste

slurry cavern has been plugged with cement, the plastic nature of the salt under strata pressure will provide an effective seal. Many large salt deposits in the United States are located near a number of the major hazardous waste generation areas, a factor which would minimize transportation and handling costs. Any solution-mined storage facility must have three characteristics for successful cavern construction:

1. a sufficient thickness of structurally sound salt at a proper depth without excess interbedded insolubles,
2. an adequate supply of raw water for leaching the salt, and
3. an environmentally acceptable and economical means of disposing of the resulting brine.

Several methods exist for storing hazardous wastes in solution-mined caverns. Three are discussed here briefly.

In a brine-balanced cavern, the product to be stored is injected with a pump, displacing brine up the well casing and to a brine holding pond. Caverns using this concept have a very long life because the range of stress on the salt is small. The main advantage of using this method for hazardous wastes is that it permits the use of very large caverns. If the hazardous waste slurry is significantly heavier than saturated brine, the waste can be injected into the top of the cavern, displacing saturated brine up the casing string. If the specific gravity of the waste is close to or less than that of the saturated brine, the waste slurry must be weighted so that it is significantly heavier than the brine and remains on the bottom of the cavern. The floating brine would then be displaced from the top of the cavern and directed to disposal areas. Contamination of the brine by the waste is possible using this method.

In an atmospheric pressure cavern, the brine is pumped out by means of a submersible pump and directed to disposal. Chemically compatible liquid and pumpable slurry wastes are then inserted into the cavern. Displaced vapors or gases are collected and either sent through a scrubber or burned in an approved flare. A cavern exposed to atmospheric pressure would be limited in size to maintain structural integrity. No brine contamination would occur, but a scrubber and flare would be required. Hazardous wastes can be mixed with a cement or polymer slurry before injection into a cavern to provide permanent solidified storage for liquid and slurry wastes, and to reduce risks from earthquakes or inadvertent drilling into a hazardous waste-filled cavern. Such a cavern would be limited in size to maintain structural integrity during the period it is exposed to atmospheric pressure.

In a gas-pressure cavern, the brine is displaced by an inert gas and injected into a remote brine disposal well. The cavern is sealed at the minimum design pressure, then liquid and slurry wastes are injected into the cavern until the inert gas reaches the maximum design pressure. Gas balancing permits the use of a smaller cavern than the brine balancing, and a larger cavern than the atmospheric method. Gas balancing eliminates the possibility of brine contamination and the need for a scrubber and flare.

Stabilization/Solidification

The terminology associated with these techniques is defined as follows: (1) Stabilization refers to those techniques which reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization. (2) Solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity.

The encapsulation may be of fine waste particles (microencapsulation) or of a large block or container of wastes (macroencapsulation). Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents, but may involve mechanically binding the wastes into the monolith. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching, and/or by isolating the wastes within an impervious capsule.[23] Most stabilization/solidification systems available today are proprietary processes involving the addition of absorbents and solidifying agents to a waste. Often the process is changed to accommodate specific types of wastes. Most processes fall within a few generic types with proprietary additives added by different companies. The exact degree of performance observed in a specific system may vary widely from its generic type, but the general characteristics of a process and its products can be discussed. Waste stabilization/solidification systems that have potentially useful application for hazardous waste include:

- Sorption
- Lime-fly ash pozzolan processes
- Pozzolan-portland cement processes

  (Pozzolan is any siliceous and aluminous substance that chemically reacts with slaked lime to form a cementitious compound.)
- Thermoplastic microencapsulation
- Macroencapsulation
- Vitrification

Sorption involves the adding of a dry, solid substance to a liquid or semi-liquid waste to take up free liquid and improve waste handling characteristics. The sorbent may hold the fluid as capillary liquid, or react chemically with

it. Common natural sorbents include:

- Soil
- Fly ash
- Bottom ash
- Cement kiln dust
- Lime kiln dust

A number of synthetic sorbents are also available, but due to their relatively higher cost, are less commonly used as solidification agents.

Sorbents, especially natural ones, are in wide use at hazardous waste landfills to eliminate free liquid and improve waste handling characteristics. In many cases, however, the sorbed wastes remain subject to leaching, and the landfill liner and leachate collection system are relied on to prevent contaminant migration. Sorbents that act like sponges and only soak up the liquids are prohibited by the RCRA amendments of 1984.

Lime-fly ash pozzolan processes involve mixing wastes with natural or artificial silicic material and hydrated lime. Natural pozzolana include some volcanic tuffs and diatomaceous earth. Artificial pozzolana include blast furnace slag, ground brick, and some fly ashes from the burning of coal.

A number of waste treatment processes employ portland cement as the solidifying agent, often with a pozzolanic material (such as fly ash) added to improve strength and increase durability. A variety of other additives, such as other forms of silica, and clays may also be employed to alter the performance of these processes. The type of portland cement can be selected to favor particular cementation reactions, thus avoiding interference from incompatible compounds.

The suspended solids in a waste slurry become incorporated into the hardened concrete matrix. Most multivalent toxic metals will be transformed into their low solubility hydroxides or carbonates by the high pH of the cement mixture. Some metal ions may become integrated into the mineral crystals within the cement. Some materials in a waste can increase the strength and durability of a waste. These include sulfides (except sodium sulfide), asbestos, and latex. A number of compounds can interfere with the solidification process. Some, such as soluble salts of manganese, tin, zinc, copper, and lead, can increase setting times and greatly decrease physical strengths. Impurities such as organic matter, silts, and some clays, can cause significant delays in setting. These impurities and other insoluble materials, fine enough to pass a No. 200 mesh sieve, can coat larger particles and weaken the waste/cement bond. Cement-fly ash solidification techniques, with or without waste-specific additives, are among the most common offered by solidification vendors. Due to their relatively higher cost, they are less commonly used than lime-fly ash techniques.

Thermoplastic microencapsulation involves mixing dried wastes with materials such as bitumen (asphalt), paraffin, polyethylene, polypropylene, or sulfur amended asphalt, and placing the mixture in some sort of container or mold. The most commonly employed material is asphalt. These techniques, developed originally for radioactive waste disposal, are adaptable to highly soluble toxic substances which are not amenable to lime or cement-based techniques. The greatest limitations to use of these techniques are relatively high cost, and the need for specialized mixing equipment and trained operators. Also, the wastes must be dried before mixing with the heated thermoplastic.

Consequently, these techniques are generally used to achieve complete containment of special waste types in cases where costs are not a seriously limiting factor.

Macroencapsulation, often referred to as jacketing, is a technique for isolating wastes by completely surrounding them with a durable, impermeable coating. One such technique involves sealing the wastes in a polyethylene or polyethylene-lined drum. Another involves drying the wastes, mixing them with polybutadiene, and compressing the mixture into a block. The block is then placed in a mold surrounded by powdered polyethylene and heated under pressure. The resultant product is a block with a thin polyethylene coating fused to it.

Another solidification technique is vitrification. Wastes are mixed with silica and heated to extremely high temperatures, and allowed to cool into a glass-like solid. A variation of this technique, using graphite electrodes driven into buried wastes, allows in-situ vitrification. All vitrification systems employ some type of hood to capture and treat the fumes and vapors given off during operation. Because these systems are very energy intensive, thus costly, they are generally considered only for radioactive or extremely dangerous wastes.

Chemical Treatment

Chemicals have the ability to alter the nature of materials and this accounts for the rather wide applicability that chemical treatment has in hazardous waste destruction. It is possible, for example, to take the pesticide, ethylene dibromide (EDB), and convert it chemically to the salt, potassium bromide (which has economic value), and the gas, acetylene. Other chemical approaches modify hazardous materials so that they become nontoxic. Glycol-based chemical reagents, for example, remove a chlorine atom from 2,3,7,8-dioxin converting the dioxin to a nontoxic adduct. Here, chemical

and biological methods can complement each other for, once a single chlorine atom is removed from the dioxin molecule, the partially-dechlorinated dioxin is much less toxic to microorganisms and is consequently subject to natural biological decomposition to harmless salts and gases. A brief review of the major chemical treatment processes follows.

Chemical Oxidation

Chemical oxidation is a process which oxidizes ions or compounds to render them nonhazardous or to make them more amenable to subsequent removal or destruction processes. Species are oxidized by the addition of a chemical oxidizing agent which is itself reduced.

Chemical oxidation has been used to treat hazardous organic and inorganic contaminants in aqueous solution. Its major use has been for treating cyanide in plating wastes. In this process, chlorine gas, chlorine dioxide, or hypochlorite (sodium or calcium) are routinely used to destroy cyanide (CN^-), which is converted to nitrogen gas (N_2) and carbon dioxide gas (CO_2). Other less common oxidants include potassium permanganate ($KMnO_4$), hydrogen peroxide, and ozone.

Potassium permanganate has been experimentally used for destruction of trace organics (including aldehydes, mercaptans, phenols, and organic acids) in aqueous hazardous waste and drinking water. It has also recently been used to treat nonchlorinated pesticides.

Cyanide destruction by chlorine oxidation is common among metal plating and finishing operations which use cyanide.

Chemical oxidation is most useful for dilute aqueous wastes. Chemical oxidants are relatively nonselective and may oxidize other compounds present in

the waste prior to oxidizing tne contaminant of concern, e.g., the cyanide or metal. As a result this process has limited application for slurries, tars, and sludges which may contain large amounts of oxidizable components.

Ozonation is another chemical oxidation process appropriate for aqueous streams which contain less than 1.0 percent oxidizable compounds. Ozone can be used to pretreat wastes to break down refractory organics before biological or other treatment. Biorefractory compounds in toluene diisocyanate, ethylene glycol, and ethylene dichloride contaminated aqueous process wastes are oxidized to a biodegradable form by ozone. Ozonation is found to improve the biotreatability of water containing styrene by transforming it to a compound such as benzoic acid. It can also be used as a polishing step after biological or other treatment processes to oxidize untreated organics.

A combination of UV radiation and ozone has been demonstrated to economically treat certain halogenated organics including aldrin, chlorinated phenols, dieldrin, endrin, ethylene dichloride, kepone, methylene chloride, PCB, DDT, and pentachlorophenol. Aldehydes, ketones, alcohols, aromatic hydrocarbons, ethers, carbonyl compounds, chlorinated aromatics (pesticides), nitroso compounds, and saturated hydrocarbon groupings are all oxidizable with ozone. Bis (2-ethylhexyl) phthalate, benzene, anthracene, benzo(a)pyrene, benzo(k) fluoranthene, pyrene, benzoic and perbenzoic acids, styrenes, and aqueous waste from petrochemical processes producing toluene diisocyanate, ethylene glycol, styrene monomers, and ethylene dichloride have also been successfully pretreated by ozonation before biological treatment.

Chemical Reduction

Chemical reduction involves the transfer of reactive electrons from one

compound to another, and is used to either render compounds nontoxic, or to enable compounds to undergo chemical destruction or physical removal. Metals, in particular hexavalent chromium, are reduced through the addition of a compatible reducing agent, for example, reduced sulfur compounds. Specific solutions' pH and agitation requirements must be met to ensure successful chemical reduction.

Chemical reduction is best applied to liquid wastes free of organic compounds. It is widely used in industry to control hexavalent chromium waste, and to remove and/or recover mercury from mercury cells used in chloralkali manufacturing. Chromium is usually reduced by sodium sulfite salts or sulfur dioxide. Iron, aluminum, and zinc have also been identified as potential chrome reducing agents. Caustic sodium borohydride ($NaBH_4$) has been commercially employed to reduce mercury to elemental form, allowing its recovery. $NaBH_4$ is also now used on a commercial scale to reduce soluble lead, including organo-lead salts from tetra-alkyl lead manufacturing aqueous wastes, and to reduce and recover silver from photographic operations.

Chemical reduction is also a common hazardous waste technology for reducing complexed or chelated metals, such as copper and nickel, found in aqueous metal plating waste. The solution pH is adjusted to break the metal-chelate bond, then the reducing agent is added to reduce the metal and precipitate it out of solution. Filtration often follows.

Chemical reduction has limited application to treatment of slurries, tars, or sludge because surface contact is difficult to achieve between reducing agent and the hazardous constituent. Solid hazardous materials must be liquified prior to treatment by reduction. Because reducing agents are not selective, organic compounds present in treated solutions will decrease destruction efficiency and may liberate offensive odors.

Neutralization

Neutralization involves combining either an acid or a base with a hazardous waste stream to adjust liquid pH to acceptable levels. Neutralization may be required prior to waste treatment to protect downstream equipment and optimize treatment performance. The pH of an acid or base should not be confused with its acidity or basicity, which is the volume of base or acid required to reach a specified pH. The final desired pH is usually between 6.0 and 9.0, and the reaction products include water, salts, and solids precipitated by pH dependent solubility reactions.

Neutralization is most commonly performed in corrosion resistant tanks, although ponds and limestone filter beds are also used. Lime, calcium hydroxide, caustic soda, soda ash, and ammonium hydroxide are common bases; sulfuric acid, hydrochloric acid, and nitric acid are common acids used for neutralization.

While relatively straightforward in theory, neutralization continues to be one of the most common processes used in the hazardous waste treatment industry.

Chlorinolysis

In the chlorinolysis process, chlorine reacts with chlorinated hydrocarbon wastes at temperatures of 500° to 800°C and pressures of 1,000 psig or greater. The reaction products include carbon tetrachloride (CCl_4), perchloroethylene, trichloroethylene, anhydrous hydrogen chloride, unreacted hydrocarbons, and unreacted chlorine. The process steps include pretreatment of the wastes by filtration and/or distillation to remove water, solid materials, and incompatible compounds which are extraneous to the process; reaction with chlorine; distillation to separate the reaction products; and absorption of the hydrochloric acid solution that is produced.

Generally, the chlorinolysis process is suitable for conversion of chlorinated wastes and residues including, but not limited to, waste from the production of pesticides, vinyl chloride, herbicides, and solvents. Thirteen pesticides which are amenable to chlorinolysis include aldrin, chlordane, DDD, DDT, ethylene dichloride, benzene hexachloride, heptachlor, lindane, o- and p-dichlorobenzene, pentac, perthane, and TCBB.[31] Wastes to be used as a feedstock should contain only hydrogen, carbon, and chlorine. The presence of other substances, such as sulfur, could result in corrosion; and phosphorus, nitrogen, or oxygen could result in the production of unwanted by-products. In addition, feed streams must contain less than five percent aromatic compounds in order to limit the reaction temperature to the design temperature. Pretreatment is required to remove undesirable compounds. Chlorinolysis is operated in a large scale requiring an adequate continuous supply of chlorinated wastes to make the process feasible.

Wet Air Oxidation

Wet air oxidation is the aqueous phase oxidation of dissolved or suspended organic or inorganic substances at elevated temperature (177° to 315°C) and pressure (300 to 3,000 psi). Elevated pressure is used to keep the water in its liquid state, allowing organic destruction to proceed at lower temperatures than would otherwise be necessary. Water serves to moderate the oxidation rate, removing excess heat of reaction.[26] Oxygen is incorporated as the oxidizing agent. Feed materials are pressurized and pumped to a heat exchanger which preheats the feed and cools the reactor vessel effluent. Additional heat as needed is added to the preheated feedstock and/or the reactor vessel. Air or oxygen is injected prior to the heat exchangers or in the reactor. Reactor

effluent not sufficiently cooled in the heat exchanger may require additional cooling. The effluent then travels through a pressure control valve to reduce its pressure to a normal atmospheric level.

After pressure let-down, the vapor and liquid components of the cooled effluent are separated. The vapor passes through an air pollution control system which may include a water scrubber and an activated carbon adsorption system or an off-gas incinerator. The aqueous effluent stream, which might contain low molecular weight organic acids, may be discharged to a subsequent treatment process for further treatment.

Wet air oxidation (WAO) converts hazardous wastes to less toxic substances. Reduced sulfur compounds, such as sulfides and mercaptans, are oxidized to inorganic sulfates; cyanides to carbon dioxide and ammonia or nitrogen gas; chlorinated hydrocarbons to hydrochloric and simple organic acids; and metals to metal salts.[29] Certain highly chlorinated aromatic organics such as pentachlorophenol, PCB's, and DDT are resistant to destruction in the conventional WAO process. However, Zimpro reports that a proprietary cocatalyst system demonstrated at bench-scale enables greater than 99.5 percent destruction of these compounds by WAO at 275°F.

Wet air oxidation can be used to oxidize any material, organic or inorganic, with an approximate COD value between 10,000 and 100,000 mg/l.[28] It is best suited to cyanide destruction and to pretreatment of organics-containing aqueous hazardous wastes too toxic for biological treatment or too dilute for incineration.[29]

This process is well established for treatment of municipal sludges and nonhazardous industrial wastes with over 180 installations in operation or under construction. Its commercial application to hazardous waste has been limited to date.

Dechlorination Processes

Dechlorination processes use chemical reagents to remove chlorine from chlorinated molecules, to break apart chlorinated molecules, or to change the molecular structure of the molecule. Metallic sodium is typically the reagent used to strip the chlorine away from constituents to form sodium chloride. Other proprietary reagents are often used in conjunction with metallic sodium to further treat the dechlorinated constituents. The majority of the dechlorination research has been aimed at the detoxification of polychlorinated biphenyls (PCB's). This research is applicable to many chlorinated organic molecules, e.g., the detoxification of 2,3,7,8-tetrachlorodibenzo-p-dioxin (referred to as dioxin).

A number of companies and research institutions have investigated dechlorination processes. Four of the more common dechlorination technologies include the Acurex process, APEG process, PPM process, and Sunohio PCBX process.

The Acurex process uses a sodium reagent with a proprietary constituent. The treatment stream is filtered prior to further treatment. After filtration, the stream is transferred to a reaction tank where it is mixed with the sodium/proprietary constituent mixture. The products of this reaction are a sodium hydroxide stream and another nontoxic effluent. The Acurex reaction process is performed under a "nitrogen blanket" so that air emissions are minimized.

The Sunohio PCBX process, unlike the Acurex process, is a continuous treatment operation. This process uses a proprietary reagent to convert the PCB molecules to metal chlorides and polyphenyl compounds.

The PPM process uses a proprietary sodium reagent to dechlorinate organic molecules. This process is a batch process. A solid polymer is generated from the reaction and this substance, although regulated, can be more easily disposed than the chlorinated organics.

The APEG process uses polyethylene glycols or their derivatives that have been reacted with alkali metals or their hydroxides. Dioxin and PCB's can be destroyed in soil using a series of reagents prepared from potassium and polyethylene glycols (KPEG), however, moisture adversely influences the rates of reaction. A heated slurry process has subsequently been developed to negate the influence of moisture. This is a batch process that is controlled at operating temperatures ranging from 75° to 150°C. The reaction products associated with this process include potassium chloride, nontoxic organics, and other dechlorinated materials.

The above described processes are applicable to many chlorinated organics such as PCB's, dioxins, solvents, and pesticides. In addition, these processes may be suitable for the treatment of other halogenated organics.

Supercritical Fluid Extraction

As in liquid-liquid extraction, an organic-containing aqueous feed is contacted with a solvent in a counter-current extraction column. The solvent is CO_2, either supercritical fluid or near-critical liquid, and the feed is an aqueous solution of organics. The resulting extract, solute in solvent, is reduced in pressure and sent to a solvent-stripping system at 40-50 atm. A CO_2 vapor stream is recovered overhead and the bottom is substantially enriched in the extracted organic.

The CO_2 vapor from the still is compressed adiabatically to extractor pressure (65 atm), increasing its temperature. From this higher temperature, heat is released by cooling and condensing the vapor in the reboiler tubes to boil-up the reboiler bottoms, and the condensed CO_2 is returned as solvent recycle to the extractor. The product, stripped of most of the CO_2 solvent, is

let down in pressure in sequential flashes. The raffinate is similary flashed, and CO_2 is recovered from both streams, recompressed, and returned to the solvent system.

A qualitative comparison can be made with two major established separation processes: distillation and normal-liquid solvent extraction. Distillation or stripping is used for separating a range of organics from water, where such organic chemicals are manufactured in aqueous systems. Examples include volatile alcohols, ketones, and the like (VOC's), which are high-volume solvents and chemicals. Other examples include heavy, high-boiling liquids from which water must be distilled. In both examples, distillation energy requirements are substantial. In normal-liquid solvent extraction, the extraction unit has minimal energy requirements. However, there is a need to separate solvent from extracted solute, and this is generally done by distillation. Such distillations normally require vaporization of the entire solvent volume, involving mixtures with low volatility and high heat of vaporization, and thus high energy costs.

Several additional benefits arise from the favorable kinetic properties of critical fluids as solvents, which may be important factors in improving process economics. The low viscosities of the solvent streams reduce pressure drops, and thus pumping requirements. Improved diffusion characteristics can lead to higher separation efficiencies in mass transfer equipment, often reducing the volume and cost of such equipment.

Supercritical water oxidation is the destruction of refractory organic compounds using supercritical water at a temperature and pressure of at least 374.2°C and 218.3 atmospheres, respectively. It is a developing technology which takes advantage of the greatly increased solubility of immiscible organics in water when an aqueous mixture reaches the supercritical state. Chlorinated

pesticides and other high molecular weight organic compounds are reported to be completely oxidized to CO_2, H_2O, and inorganic salts under these conditions.[30] This reaction has been performed in a pressurized reactor.

Application of this technology to the following wastes seems possible once a commercial-scale facility begins operation:

- refractory organics including solvents, chlorinated pesticides, and dioxins
- cyanides

The limitation of this process is that no commercial-scale supercritical unit is currently operating. Until such time as an installation becomes operative and destruction efficiencies and system reliability are verified, this technology must be viewed as experimental.

REFERENCES

1. Congress of the U.S.A. "The Hazardous and Solid Waste Amendments of 1984," PL 98-616, Washington, D.C., Nov. 1984.
2. American Institute of Chemical Engineers. "Technological Need for Improved Management of Hazardous Waste." Hazardous Waste Task Force Report, 1901 L Street, N.W., Washington, D.C. 20036, Feb. 1986.
3. U.S. Environmental Protection Agency. "Ground-Water Protection Strategy." U.S. EPA Office of Ground-Water Protection, Washington, D.C., Aug. 1984.
4. Shuckrow, Alan J., Andrew P. Pajak, and C. J. Touhill. Management of Hazardous Waste Leachate. SW 871, U.S. Environmental Protection Agency, Washington, D.C., 1983.
5. Goode, Daniel J. and Patricia A. Smith. Procedure for Modeling Flow Through Clay Liners to Determine Required Liner Thickness. Draft Report, EPA 530-SW-84-001, U.S. Environmental Protection Agency, Washington, D.C., 1984.
6. Roy, W. R. and R. A. Griffin, S. F. J. Chou and I. G. Krupac. Batch Soil Procedure to Design Clay Liners for Pollutant Removal. Draft Report, U.S. Environmental Protection Agency, 1985.
7. Roberts, D. W. Soil Properties, Classification and Hydraulic Conductivity Testing. Draft Report SW-925, U.S. Environmental Protection Agency, Washington, D.C., 1984.
8. Haxo, Henry E. Lining of Waste Impoundment and Disposal Facilities. SW-870, U.S. Environmental Protection Agency, Washington, D.C., 1983.

9. Moore, Charles A. Landfill and Surface Impoundment Performance Evaluation. SW-869, U.S. Environmental Protection Agency, Washington, D.C., 1983.

10. Public Comment Draft: Construction Quality Assurance for Hazardous Waste Disposal Facilities. EPA-530-SW-85-021, U.S. Environmental Protection Agency, Washington, D.C., 1985.

11. _____, "Permeability and Groundwater Contaminant Transport." ASTM STP 746, Philadelphia, PA, 1981.

12. _____, "Hydraulic Barriers for Soil and Rock." ASTM STP 874, Philadelphia, PA, 1985.

13. Acar, Y. B. and R. K. Seals. "Clay Barrier Technology for Shallow Land Waste Disposal Facilities." Hazardous Waste, Vol. 1, No. 2, pp. 167-181, 1984.

14. Bowders, John J., D. E. Daniel, G. P. Broderick, and H. M. Liljestrand. "Methods for Testing the Compatibility of Clay Liners with Landfill Leachate." Proceedings of the Fourth International Symposium on Hazardous and Industrial Solid Waste Testing, ASTM STP 886, pp. 233-250, 1986.

15. Brown, K. W. and D. C. Anderson. "Effects of Organic Solvents on the Permeability of Clay Soils." U.S. Environmental Protection Agency, EPA 600/2-83-016, Cincinnati, OH, 1983.

16. Haxo, Jr., H. E., R. S. Haxo, N. A. Nelson, R. M. White, and S. Dakessian. "Liner Materials Exposed to Hazardous and Toxic Wastes." EPA 600/2-84-169, Cincinnati, OH.

17. Daniel, D. E. and S. J. Trautwein. "Field Permeability Test for Earthen Liners." Proceedings, In-Situ '86, ASCE Specialty Conference on Use of In-Situ Tests in Geotechnical Engineering, Blacksburg, VA, 1986.

18. Lutton, R. S. Evaluating Cover Systems for Solid and Hazardous Waste. U.S. Environmental Protection Agency, Report SW-867, Washington, D.C., 1982.

19. McAneny, Colin C. and Allen W. Hatheway. Design and Construction of Covers for Uncontrolled Landfill Sites. U.S. Environmental Protection Agency, Draft Report, 1985.

20. Schroeder, P. R., J. M. Morgan, T. M. Walski, and A. C. Gibson. Hydrologic Evaluation of Landfill Performance (HELP) Model. U.S. Environmental Protection Agency, Draft Report, EPA 530-SW-84-009, EPA 530-SW-84010, U.S. Environmental Protection Agency, Washington, D.C., 1984.

21. _____, "The CMA Hazardous Waste Survey for 1981 and 1982." Chemical Manufacturers Association, Washington, D.C., 1983.

22. Stone, R. B., K. A. Covell, T. R. Moran, L. W. Weyand, and C. U. Sparkman. "Using Mined Space for Long-Term Retention of Nonradioactive Hazardous Waste." Vols. 1 & 2, U.S. Environmental Protection Agency, EPA 600/2-85-021, Cincinnati, OH, 1985.

23. Cullinane, M. J. and L. W. Jones. "Technical Handbook for Stabilization/ Solidification of Hazardous Waste." U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, 1985.

24. _____, "Hazardous Waste Treatment Technology." U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, 1986.

25. _____, "Treatability Manual," Volumes 1-5, U.S. Environmental Protection Agency, EPA 600/2-82-001, Washington, D.C., Jan. 1983.

26. Kiang, Y-H and A. Metry. "Hazardous Waste Processing Technology." Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1982.

27. DeRenzo, D.J. (Editor). "Unit Operations for Treatment of Hazardous Industrial Wastes." Noyes Data Corporation, Parks Ridge, NJ, 1978.

28. _____, "Alternative Technology for Recycling and Treatment of Hazardous Waste." California Department of Health Services, Sacramento, CA, July 1984.

29. Canney, P.J. and P. T. Schaefer. "Detoxification of Hazardous Industrial Wastewaters by Wet Air Oxidation." 1983 Spring AICHE Meeting, Houston, TX, March 1983.

30. Josephson, J. "Supercritical Fluids." Environmental Science and Technology, 16(10): 548A-551A, 1982.

31. GCA Corporation - Technology Technical Assessment of Treatment Alternatives for Wastes Containing Halogenated Organics, U.S. Environmental Protection Agency, Cincinnati, OH, Oct. 1984.